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AN ATR-UV SENSOR FOR ON-LINE MONITORING OF SULFIDE, ALKALI, AND CARBONATE IN KRAFT MILL RECAUSTICIZING OPERATIONS

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ABSTRACT

This paper describes an ATR-UV sensor that provides rapid and simultaneous determination of sulfide, effective alkali, and carbonate in kraft liquors. The results of two on-site mill trials on the measurement of the three component concentrations show good agreement between the ATR-UV method and the standard off-line ABC titration method. The ATR-UV technique is very simple to perform and can be used as on-line process control.

INTRODUCTION

Reliable, rapid, accurate, and complete on-line analysis of white and green liquor compositions, i.e., hydroxide (or alkali), carbonate, and sulfide, is the key to better control in recausticizing operations to produce high quality white liquor to control pulp quality and reduce operation dead load. Unfortunately, most pulp mills all over the world rely on a classical offline titration method, i.e., ABC titration [1], to determine the concentration of alkali, carbonate, and sulfide in white and green liquors, which cannot provide timely information and is performed every 2 to 4 hours in mill practice. Therefore, recausticizing operations are not well controlled, resulting in the loss of productivity and high energy cost due to unnecessary dead load and low recausticizing efficiency.

Non-titrametric based sensors, such as conductivity sensors [2-4] and conventional ultraviolet (UV) spectroscopy [5] have been developed for kraft white and green liquor analysis. However, these sensors can only provide single component analyses, such as hydroxide using a conductivity sensor [2-4]. Sample dilution by a factor of 1000 is required when using conventional UV technique [5] to measure sulfide in green and white liquors due to saturation in absorption. A high dilution ratio not only compromises the measurement accuracy but also requires a high degree of dissolved oxygen removal because the sulfide in diluted solution can be easily oxidized by the dissolved oxygen. NIR spectroscopy [6, 7] has demonstrated the potential for simultaneous analysis of alkali, sulfide, and carbonate in white, green, and black liquors. However, the accuracy of any NIR spectroscopy is always compromised by the spectral interference from the absorption of water in the entire NIR range. Moreover, there are no identifiable absorption peaks or bands corresponding to the species of interest in the kraft liquors, i.e., sulfide, hydroxide, and carbonate, in the NIR absorption spectra. Therefore, the species concentration determination can only rely on a multivariate partial least-squares analysis, which not only requires a complex software package for data reductions but also involves very sophisticated calibration through a software training process to obtain a spectral database using a range of samples of known composition.

Attenuated total reflection (ATR) spectroscopy was developed in the 1960s by Fahrenfort [8] and Harrick [9]. Because the absorption pass-length in ATR spectroscopy is greatly reduced to the order of micrometers, it is particularly applicable to the analysis of very concentrated samples without dilution, such as kraft white and green liquors. Leclerc and Hogikyan [10] applied ATR-infrared (IR) technique for kraft liquor analysis. However, the ATR-IR technique is not capable of detecting sulfide, an important parameter in kraft recausticization.

Chai et al. successfully demonstrated an ATR-UV technique [11] and performed in-line simultaneous monitoring of sulfide and polysulfide in a lab-scale electrochemical production of polysulfide from a synthetic kraft white liquor [12]. However, the synthetic white liquors that Chai [12] used did not contain carbonate. The present authors demonstrated simultaneous measurements of sulfide, alkali, and carbonate in kraft liquors by ATR-UV spectroscopy in our laboratory [13]. A multivariate partial least-squares analysis procedure was used for calibration because the refractive index of kraft liquor can affect absorption optical path length; and, therefore, the absorption spectral intensities. It is of great interest to simplify the calibration procedure and data reduction process for practical applications. The objective of the present study is to develop and demonstrate a linear calibration and data reduction procedure to simplify the ATR-UV technique for on-line and simultaneous measurements of sulfide, alkali, and carbonate in kraft mills.

METHODOLOGY

We derived the ATR absorption spectral intensity, A_λ, at the given wavelength in a previous study [13] based on the basic ATR principles in the literature [8, 9, 14]. For an ATR system with z reflections, we found

$$A_\lambda = k \cdot z\left[(\varepsilon_1 C_1 + \varepsilon_2 C_2 + \ldots + \varepsilon_n C_n) \cdot b_{eff}(C_1, C_2, \ldots C_n, \lambda)\right] \quad (1)$$

where k is the instrument response function of the ATR system, which includes the responses of the detectors, optical components, and the slit transfer function of the spectrometer. b_{eff} is the effective optical path length of the ATR probe. ε_i and C_i are the absorption coefficient and molar concentration of species i in the liquor, respectively. λ is the wavelength of interest. If the variation of the effective optical path length is not significant and can be neglected, then, Eq. (1) can be simplified as

$$A_\lambda = f_1^\lambda \cdot C_1 + f_2^\lambda \cdot C_2 + \ldots + f_n^\lambda \cdot C_n \quad (2)$$

where $f_i^\lambda = z b_{eff} \cdot k_i \varepsilon_i$ are wavelength dependent calibration constants.

EXPERIMENTAL

A laboratory bench scale ATR-UV system was used in this mill trial study. Figure 1 shows the schematic of the ATR-UV system along with the kraft liquor flow loop for on-line

measurements. The system consists of a circular cross-section ATR flow cell (model TNL-120H23-3, Axion, CA, USA) with one path, a peristaltic pump (RP-1, Rainin, Emeryville, CA, USA), and a UV/Vis spectrophotometer (UV-8452, Hewlett-Packard, now Agilent Technologies, CA, USA).

Mill trials were conducted at Cantonment, FL, USA, Champion International, and Camas, WA, Fort-James, USA. Hot liquor samples were collected from the mill recausticizing unit and cooled to room temperature in tap water. The sample was introduced directly into the ATR-UV system reservoir without dilution or treatment and circulated to the ATR flow cell by the peristaltic pump for absorption measurements. Although direct, on-line analysis was not attempted to avoid complications in direct interfacing of the hot liquor from the recausticizing plant to the bench scale ATR-UV system, representative liquor sampling was achieved through proper handling in sample collection. Furthermore, direct comparison can be made between the ATR-UV and ABC titration measurements using the same sample in this approach. A computer system (HP Chemstation) acquires the absorption spectral data from the spectrometer at a rate of one spectrum per second and processes the data.

RESULTS AND DISCUSSION

ATR-UV Spectra of a Kraft White and Green Liquor

Figure 2 shows the typical absorption spectra of a kraft white and green liquor as measured by the ATR-UV system. As we demonstrated in our previous study [13], sulfide ions (HS^-) absorb at about 230 nm, the hydroxide ions (OH^-) absorb below 200 nm, and carbonate also absorbs below 200 nm. In aqueous solutions of inorganic salts, such as a kraft white or green liquor, the refractive index of the liquor is generally proportional to the total salt concentration.

If there is a large variation of total salt concentration, the refractive index of the process liquor will be significantly affected, causing a large variation in the optical path length in ATR measurements; and, therefore, the ATR-UV spectra. Under this unusual circumstance, a multivariate partial least-squares calibration procedure and data reduction process has to be used for quantitative analysis. In most kraft mill operations, the total salt concentration generally does not change significantly. Minor fluctuations, e.g., < 5%, do not lead to a significant change in the refractive index of the liquors based on our laboratory refractometry measurements. Therefore, the absorption optical path length can be assumed as a constant and a simple linear calibration procedure can be used in ATR-UV spectroscopy.

The Linear Calibration Procedure

Many minor process species, e.g., sulfate and thiosulfate, have absorption in the far UV range. Therefore, the presence of the minor species can affect the accuracy of the ATR-UV measurements, especially for carbonate in white liquor where its concentration is low. Furthermore, nonabsorbing minor species can contribute to the refractive index of the liquor, thereby, altering the absorption path length and affecting the ATR-UV spectrum. To minimize the effects of these minor species, it is important to use a liquor from the same site where the ATR-UV system is intended to be used for calibration.

According to Eq. (2) simple linear calibration can be conducted. Based on the spectroscopic data reported in our previous work [13], carbonate contribution to the absorption at > 200 nm can be neglected. Therefore, two simple linear equations to calibrate sulfide and EA, (the concentration of total hydroxide ions in the liquor) can be obtained using the absorption at the wavelength of 230 and 200 nm, respectively:

$$C_{Na_2S} = k_1 A_{230} \tag{3}$$

and

$$C_{EA} = k_2 A_{200} \tag{4}$$

where C is the concentration of a given chemical, k_1 and k_2 are calibration constants, and A_j is the adsorption spectral intensity at a given wavelength j nm. Carbonate concentration can be found using the absorption at 197 nm with the correction for the contribution from hydroxide ions:

$$C_{Na_2CO_3} = k_3 (A_{197} - k_4 C_{EA}) \tag{5}$$

The success of the linear calibration Eqs. (3) to (5) has been demonstrated in our previous study [15].

The Spectral Derivative Linear Calibration Procedure

Spectral baseline shift is a common problem in spectroscopic techniques, especially in the practical process environments. It is caused by many factors, such as temperature fluctuation, light scattering by the particles in the process solution, and stability of the electronics of the instrument. The random spectral baseline shift can be a major error source in using the NIR technique [6, 7] for kraft liquor analysis because it is very difficult to recalibrate when the spectral changes are random using a multivariate partial-squares fit calibration procedure. The present ATR-UV technique can easily minimize the error caused by the random baseline shift by using a spectral derivative analytical technique because the absorption peaks or bands of the species of interest are clearly defined.

Figure 3 shows the derivative spectra after taking the first derivative of the spectra shown in Fig. 2 with respect to the wavelength. Any random spectral changes including baseline shift (except spike type of spectral variations) can be effectively minimized in the derivative spectra. Calibration equations for the concentrations of sulfide and EA can be established using the derivative absorption values at the wavelengths of 238 and 200 nm, respectively:

$$C_{Na_2S} = k_5 \dot{A}_{238} \tag{6}$$

and

$$C_{NaOH} = k_6 \dot{A}_{200} \tag{7}$$

where $\dot{A}_j = dA/d\lambda|_{\lambda=j}$ is the derivative absorption spectral intensity with respect to wavelength at wavelength j. However, it is difficult to quantify carbonate using the derivative spectra because of the spectral contribution from the absorption of hydroxide ions. The effect of baseline shift on carbonate analysis is corrected differently by subtracting the absorption at 270 nm (baseline) from that at 197 nm, and Eq. (5) becomes:

$$C_{Na_2CO_3} = k_7 [(A_{197} - A_{270}) - k_8 C_{EA}] \tag{8}$$

We used a mixture of mill white and green liquors to make a set of modified liquor through addition of sulfide, hydroxide, and carbonate to calibrate Eqs. (6) to (8) for sulfide, EA, and carbonate determination. The concentration ranges of the modified liquors covers the possible concentrations of these species in the mill process liquors based on previous operating experiences. Figure 4 shows the calibration results for sulfide, EA, and carbonate, respectively. Linear regression analysis of the data indicates that the absorption data of sulfide, EA, and carbonate fit three linear equations very well with $k_5 = 5013$, $k_6 = 2839$, and $k_7 = 1768$ and $k_8 = 0.00407$.

Based on the concentrations of these three species that were calculated using Eqs (4), (5), and (6), other process parameters, e.g., TTA, AA, sulfidity and efficiency of causticizing can be calculated.

Mill Trial Applications

A 50-hour mill trial was conducted at Cantonment mill. The liquor from the first causticizer was analyzed by both the ATR-UV and ABC titration methods. The concentrations of EA, sulfide, and carbonate in the liquor from these two methods were compared as shown in Fig. 5. It was found that the concentration of the three components in the process liquor did not change significantly during the trial period. However, some small concentration fluctuations of these components were observed. The results indicate that ATR-UV measurements agree well with the ABC titration measurements. Relatively larger data scattering was observed in the ABC-titrated results of all three components primarily due to the measurement accuracy of the method. The largest deviation between these two methods in the data sets occurred about 14 hours into the trial when samples used for titration were cooled down before titration. The causticizing reactions continued to proceed during the cooling process, resulting in higher EA concentrations as shown.

A separate mill trial was conducted at Camas using borate autocausticizing operations. The borate mass fraction in the liquor (dry basis) was gradually increased from 0 to 5%. Because borate does not have an absorption in the UV range and the effect of borate on effective optical path length is negligible under a borate charge of less than 25% based on our laboratory study [15], the effect of borate on ATR spectroscopy can be ignored, and the simple linear calibration discussed in this study can be adopted. It was found that the ATR-UV measured EA concentration agrees well with that obtained by the modified ABC titration method (using boron concentration measured by atomic absorption spectroscopy) during the entire trial. The sulfide and carbonate concentrations measured by the two methods showed a little larger difference, especially toward the end of the three-day period. This difference is mainly due to the fact that the boron correction procedure adopted in the modified ABC titration method uses the same boron value measured once a day in this trial, even though the borate concentration in the process liquor was gradually accumulated throughout the trial. Furthermore, the weak alkali, sodium borate, can affect the titrated values of sulfide and carbonate, which may not be corrected using the modified ABC titration method. It can be seen that the standard deviation of the titration data is much higher than that of the ATR-UV data, especially the sulfide concentration. It should be pointed out that the reproducibility of the sulfide concentration determined by titration during the trial was not very high, about 100 ± 10%. The data clearly show that the ATR-UV method eliminated the human operator errors that occurred in the titration method.

CONCLUSION

This work successfully demonstrated the applicability of an ATR-UV sensor for determining the concentrations of sulfide, EA, and carbonate in kraft white liquors. The results obtained from two mill trials indicate that the ATR-UV method agrees well with the standard ABC titration method.

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REFERENCES

1. Pulp and Paper Manufacture, Vol 1: The Pulping of Wood. Ed: MacDonald, R.G., 2nd Ed., McGraw-Hill, New York, 1969, p563.
2. BERLELSEN, P.M. and SVENSSON, J.-O., "Sensor-Based Causticizing Control," *Tappi J.* **69**(8): 72, 1986.
3. DORRIS, G.M. and ALLEN, L.H., "Conductivity Sensors for Slaker Control: Part I – Laboratory Results," *J. Pulp and Paper Sci.*, **15**(4): J122, 1989.
4. PAULONIS, M.A. and KRISHNAGOPALAN, G.A., "Kraft Liquor Alkali Analysis Using In-Situ Conductivity Sensor," *TAPPI J.*, **73**(1): 205, 1990.
5. PAULONIS, M.A. and KRISHNAGOPALAN, G.A., "Kraft White and Green Liquor Composition Analysis; Discrete Sample Analyzer," *J. Pulp & Paper Sci.*, **20**(9): J254, 1994.
6. HODGES, R.E. and KRISHNAGOPALAN, G.A., "Near-infrared Spectroscopy for On-line Analysis of White and Green Liquors," *TAPPI J.*, **82**(9): 101, 1999.
7. HODGES, R.E. and KRISHNAGOPALAN, G.A., "Near-infrared Spectroscopy for On-line White and Black Liquor Analysis," *Proceedings of the 1999 TAPPI Pulping Conference*, p1097, 1999.
8. FAHRENFORT, J., "Attenuated Total Reflection: A New Principle for the Production of Useful Infrared Spectra of Organic Compounds." *Spectrochim. Acta*, **17**:698, 1961.
9. Harrick, N.J., "Internal Reflection Spectroscopy," John Wiley & Sons, NY, 1967.
10. LECLERC, D.F. and HOGIKYAN, R.M., "Rapid Determination of Effective Alkali and Dead-Load Concentrations in Kraft Liquors by Attenuated Total Reflection Infrared Spectrometry, " *J. Pulp and Paper Sci.*, **21**(7): J231, 1995.
11. CHAI, X.-S., "Process Analytical Chemistry Applied to Liquors in the Pulping Industry: Monitoring of Sulfur Species and Lignin." Ph.D. Dissertation, Royal Inst. of Tech. (KTH), Sweden, ISBN 91-7170-653-4, 1996.